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1. Glass research
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ALKALI MOBILITY AND MECHANICAL RELAXATION IN MIXED-ALKALI SILICATE GLASSES

BY

JAMES WILLIAM FLEMING JR., 1947-

A

THESIS

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ABSTRACT

Internal friction and sodium and potassium self-diffusion coefficients for $(1-X)Na_2O \cdot XK_2O \cdot 3SiO_2$ glasses were measured. Alkali diffusion was measured between 300 and 500°C using radioactive isotopes and a thin-sectioning technique. Internal friction was measured from room temperature to 500°C, 0.1 to 2000 Hz. Comparison between alkali diffusion and internal friction data for Na-K glasses with those for other mixed-alkali glasses shows that the mixed-alkali peak is related to alkali mobility. It is concluded that the mechanism for mixed-alkali internal friction is a cooperative rearrangement of dissimilar alkali ions, with the slower moving ion controlling the rate of reorientation.

ACKNOWLEDGEMENT

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I. INTRODUCTION

When a second alkali is added to a glass, a large internal friction peak that is absent in single alkali glasses appears.[1-4] The mechanism proposed for this mixed-alkali internal friction involves a stress-induced cooperative rearrangement of dissimilar alkali ions,[4-7] which together form an elastic dipole. This model implies that the magnitude of the mixed-alkali peak should be related to the relative mobilities of the alkali ions.

To examine the model in greater detail, McVay and Day[7] measured alkali self-diffusion and internal friction in (1-X) $Na_2O \cdot XRb_2O \cdot 3SiO_2$ glasses. They found that the magnitude of the mixed-alkali peak is a maximum in that composition where the Na and Rb diffusion coefficients (mobilities) are equal.

K.K. Evstropév[8] measured the self-diffusion coefficients of Na^{22} and K^{42} in (1-X) $Na_2O \cdot XK_2O \cdot 4SiO_2$ glasses at 415°C and found that the alkali self-diffusion coefficients were equal at X=0.77. However, the maximum magnitude for the mixed-alkali peak as measured at 125°C occurred at X=0.63 (see Appendix B). This discrepancy suggested that either the agreement between the alkali mobility and magnitude for the mixed-alkali peak in (1-X) $Na_2O \cdot XRb_2O \cdot 3SiO_2$ was a coincidence, or the composition at which the alkali diffusion coefficients are equal is

temperature dependent. Such a temperature dependence has been reported by Lacharme[9] in a mixed Na-K lime silicate glass and by Evstropév and Pavlovski[10] in a mixed Na-Rb germanate glass.

The present investigation of internal friction and alkali diffusion was undertaken to determine if the relations between alkali self-diffusion and internal friction as found in the $(1-X)Na_2O \cdot XRb_2O \cdot 3SiO_2$ glasses applies in general to all mixed-alkali glasses. It was also desired to find whether the composition at which the alkali diffusion coefficients are equal is dependent upon temperature.

The $(1-X)\ Na_2O \cdot XK_2O \cdot 3SiO_2$ glasses were studied because of the availability of internal friction data[5] and of diffusion measurements on related Na-K glasses.[8] Also, these glasses contain the same total alkali content as those studied by McVay and Day,[7] 25 mole percent, so direct comparisons could be made between the internal friction and alkali diffusion coefficients in different mixed-alkali systems. It was felt that comparisons between different mixed-alkali systems would provide a better understanding of the mixed-alkali internal friction peak.

II. EXPERIMENTAL

A. Glass Preparation

The batch compositions of the glasses studied are listed in Table I. They were prepared from reagent grade Na_2CO_3, K_2CO_3, and potter's flint (99.98% SiO_2). The glasses were melted in platinum crucibles in an electric furnace open to the atmosphere. Each melt was held at 1500°C for approximately five hours and stirred several times to insure homogeneity. Fibers approximately 0.5 mm in diameter and rectangular bars 1.3 x 1.3 x 15 cm were obtained from the bubble free melt. The specimens used for internal friction and diffusion measurements were annealed at the temperatures shown in Table I.

B. Diffusion

Radioactive isotopes, Na^{22} ($t_{1/2}$=2.62 yrs.) and K^{42} ($t_{1/2}$=12.4 hrs.), were used to determine the alkali self-diffusion coefficients. Glass samples approximately 1.3 x 1.3 x 0.3 cm were cut from the annealed rectangular bars and polished. The desired isotope was then evaporated on one end of the sample in a vacuum evaporator. The plated samples were heat-treated in an electric furnace, open to the atmosphere, between 300 and 500°C for periods from 3 to 48 hrs. Diffusion of the radioactive tracer into the glass was measured using the thin sectioning and counting technique described by McVay.[7]

TABLE I

Composition[+] and Heat-Treatment Temperatures

Molar Composition			Heat-Treatment Temp. (± 5°C)	Density (g/cm^3) (± .001 g/cm^3)
Na_2O	K_2O	SiO_2		
1.00*	0.00	3.00	515	2.432
0.60*	0.40	3.00	490	2.443
0.40	0.60	3.00	490	
0.35	0.65	3.00	495	
0.30*	0.70	3.00	495	2.433
0.00*	1.00	3.00	545	2.423
0.45	0.55	4.00	495	
0.35	0.65	4.00	500	
0.25	0.75	4.00	510	
0.15	0.85	4.00	520	

* Diffusion measured in these glasses

+ The compositions listed in this table are the batch compositions for the glasses.

The section thickness varied from 5-30 microns and the total depth of penetration varied from 100-300 microns.

Diffusion of the radioactive tracer follows the thin film solution:

$$A_i = (A_o/\sqrt{\pi Dt}\,)\ \exp\ (-X_i^2/4Dt) \qquad (1)$$

where X_i is the distance from sample-isotope interface, A_i is the specific activity at distance X_i, t is the time of diffusion, A_o is the original activity at $X_i = 0$, $t = 0$, and D is the diffusion coefficient. Diffusion measurements were made simultaneously on duplicate samples of the same composition. Diffusion coefficients determined in this study agree favorably with those in the literature, Table II.

C. Internal Friction

Internal friction was measured using an inverted torsion pendulum and a resonance technique based on Förster's method.[11] These are the same equipment and techniques described by Shelby[12] and Moore.[13] Some of the internal friction data needed for this study had been obtained previously by Shelby and Day[5] using these techniques.

Internal friction is calculated from:

$$Q^{-1} = 1/n\pi\ \ln\ (\text{amplitude ratio})^* \qquad (2)$$

*This can also be the velocity ratio

TABLE II

Comparison of Measured Diffusion Coefficients With Those Found in Literature

Glass	Measurement		Diffusion Coefficient cm^2/sec	
	Temp (°C)	Alkali	Literature	Present Technique
25 $Na_2O \cdot 75SiO_2$	415	K	2.0×10^{-10} (8)	2.47×10^{-10}
25 $K_2O \cdot 75SiO_2$	415	Na	8.4×10^{-10} (8)	8.2×10^{-10}
25 $Na_2O \cdot 75SiO_2$	350	Na	2.75×10^{-9} (18)	2.93×10^{-10}

where Q^{-1} is the internal friction, n is the number of cycles, and the amplitude ratio is the ratio of the amplitude of periodic specimen motion on the zeroth cycle and the nth cycle.

The apparent activation energy for internal friction was calculated from the equation:

$$E_a = R \left(\frac{\ln f_1 - \ln f_2}{1/T_2 - 1/T_1}\right) \qquad (3)$$

where T_1 and T_2 are the temperatures of the peak maximum at frequencies f_1 and f_2 respectively.

The activation energy was obtained from a least squares fit of measurements made at three frequencies ranging from 0.4 to 1800 Hz. The error is estimated as ± 1 Kcal.

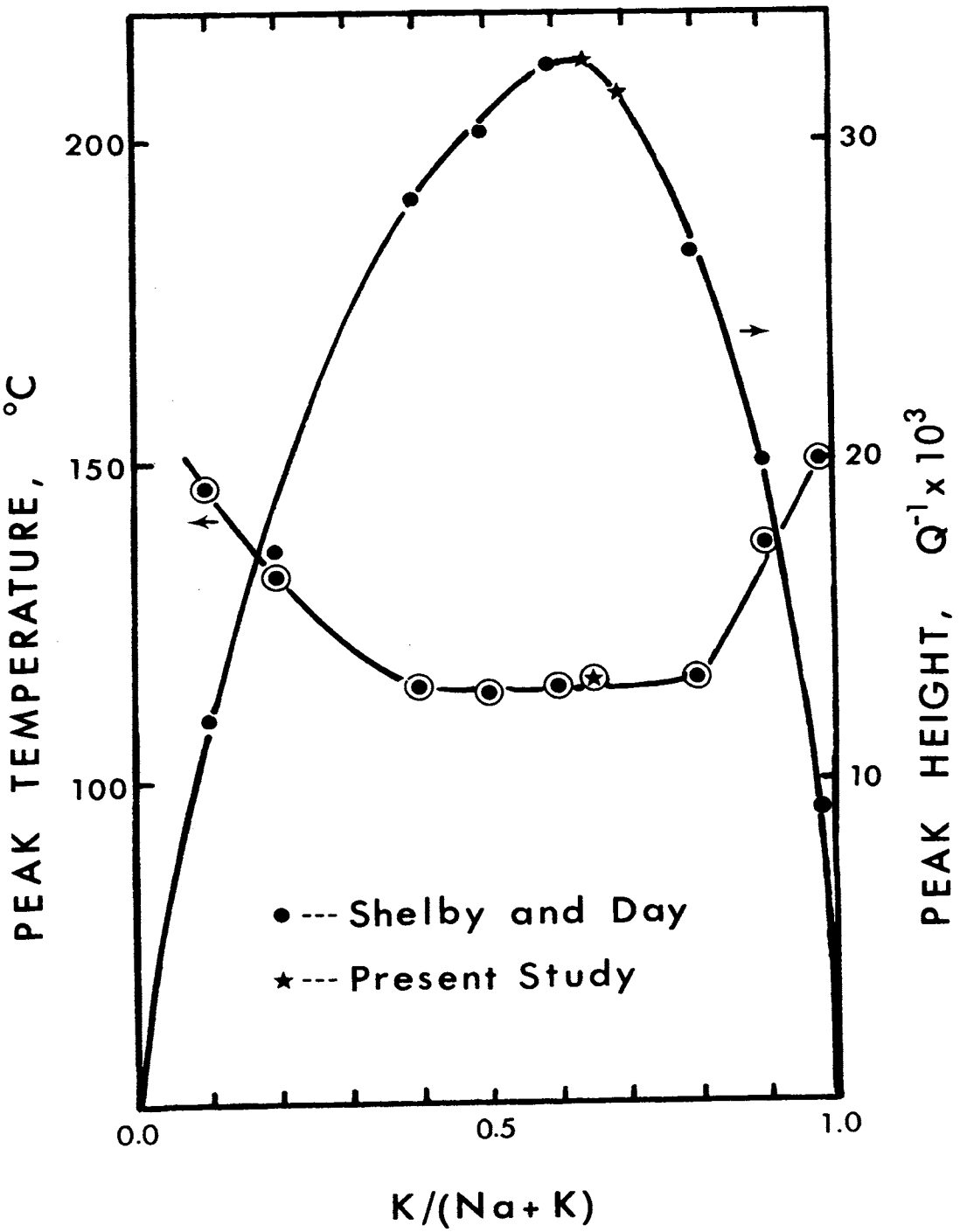

Figure 1. Temperature and Height Above Background for the Mixed-Alkali Peak in (1-X) $Na_2O \cdot XK_2O \cdot 3SiO_2$ Glasses, Frequency = 0.4 Hz.

III. RESULTS

A. Internal Friction

In a previous study[5] of the $(1-X)Na_2O \cdot XK_2O \cdot 3SiO_2$ glasses, the maximum magnitude for the mixed-alkali peak was reported to be at X = 0.60, for measurements at 0.4 Hz. At this frequency the peaks appeared at approximately 115°C. With the additional internal friction data from the present study, the composition at which the mixed-alkali peak is at a maximum was located more accurately at X = 0.65, Figure 1. Increasing the frequency of internal friction measurements to 1800 Hz. raised the temperature of the mixed-alkali peak to about 240°C. The high frequency measurements indicated that the maximum peak height also occurred at X = 0.65, Figure 2. Internal friction data are given in Table III. The difference in peak height at high and low frequencies is a consequence of the measurement techniques.[13]

B. Diffusion

Between 300 and 500°C, the self-diffusion coefficients for sodium and potassium fit the Arrhenius equation:

$$D = D_o \exp(-E/RT) \qquad (4)$$

where D is the diffusion coefficient, D_o is a pre-exponential factor, E is the activation energy, and T is the absolute temperature. Typical graphs of log D vs. 1/T for

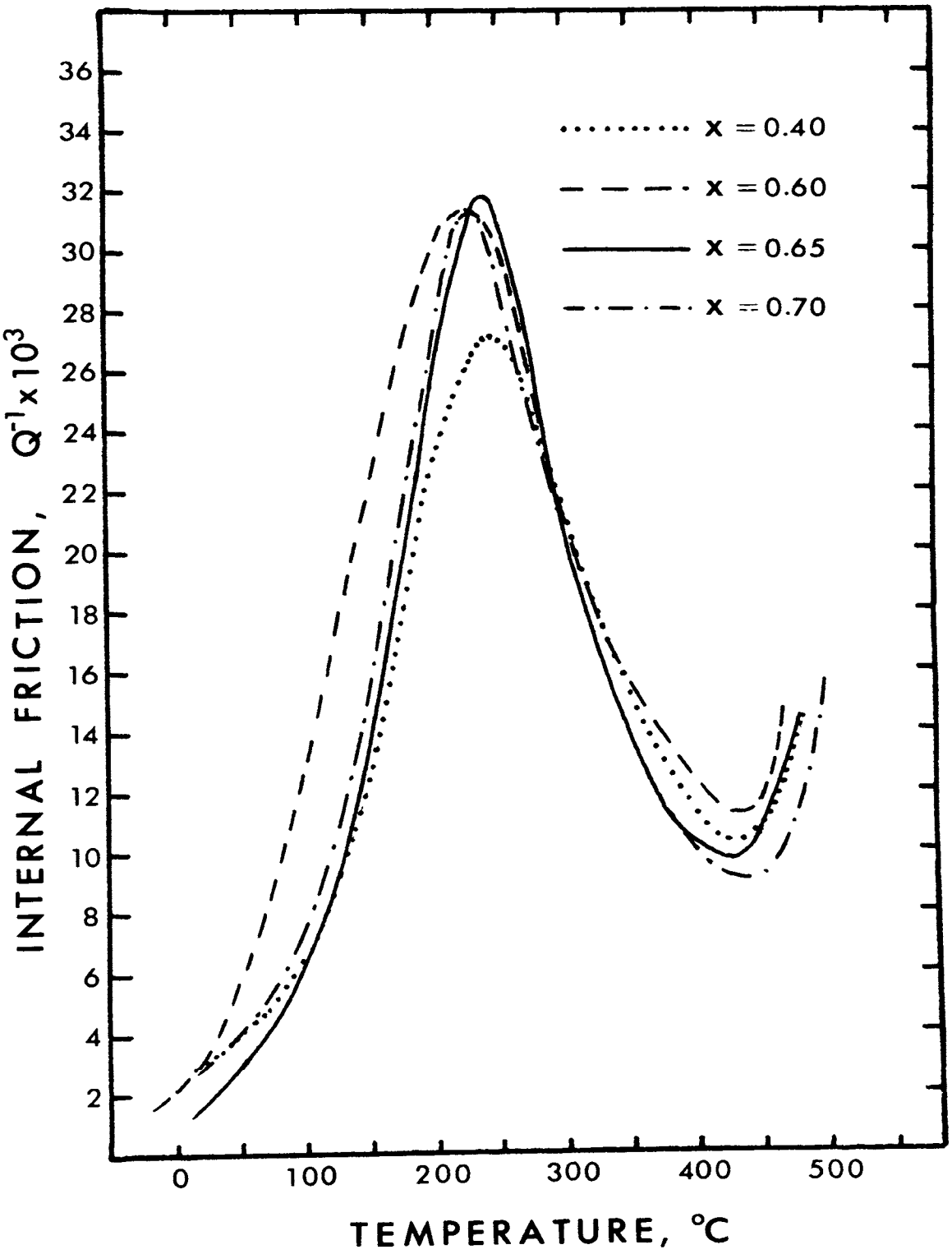

Figure 2. Internal Friction Curves for the (1-X) $Na_2O \cdot XK_2O \cdot 3SiO_2$ Glasses, Frequency = 1800 Hz.

TABLE III

Mixed-Alkali Peak Temperature, Frequency, Height Above Background, and Activation Energy

Glass	Mixed Peak		Peak Height (10^3)	Activation Energy Kcal/mole
	Temp (°C)	Frequency (Hz)		
$(1-X)Na_2O \cdot XK_2O \cdot 3SiO_2$				
X = .10	146 ± 2*	0.400	12.0 ± 0.2	
X = .20	132 ± 2*	0.400	17.2 ± 0.2	
X = .40	115 ± 2*	0.400	28.2 ± 0.2	25.8 1
	128 ± 2	1.240		
	245 ± 5	1701	23.0 ± 0.2	
X = .50	114 ± 2*	0.400	30.3 ± 0.2	25.8 ± 1.5*
X = .60	115 ± 2*	0.400	32.4 ± 0.2	
	225 ± 5	1701	27.2 ± 0.2	
X = .65	116 ± 2	0.400	32.6 ± 0.2	26.2 ± 1
	125 ± 2	1.044		
	242 ± 5	1701	27.8 ± 0.2	
X = .70	111 ± 2	.294	31.5 ± 0.2	
	232 ± 5	1690	27.4 ± 0.2	
X = .80	116 ± 2*	0.400	26.5 ± 0.2	
X = .90	137 ± 2*	0.400	20.0 ± 0.2	
X = .98	150 ± 3*	0.400	9.1 ± 0.3	
$(1-X)Na_2O \cdot XK_2O \cdot 4SiO_2$				
X = .55	115 ± 2	0.760	24.4 ± 0.2	
X = .65	125 ± 2	0.782	24.8 ± 0.2	
X = .75	123 ± 2	0.890	23.0 ± 0.2	
X = .85	126 ± 2	0.875	21.1 ± 0.2	

* Measured by Shelby and Day

Na^{22} and K^{42} in (1-X) $Na_2O \cdot XK_2O \cdot 3SiO_2$ glasses are shown in Figures 3 and 4, respectively. Self-diffusion coefficients for various temperatures, and the activation energies and pre-exponential factors for sodium and potassium self-diffusion, as calculated from equation 4, are given in Table IV.

Table IV and Figure 6 include calculated data for 250°C. It was not possible to measure the potassium self-diffusion at this temperature using the sectioning technique due to the short half-life of K^{42}. The 250°C data were included to emphasize the trend in the diffusion data and to consociate the temperature ranges of internal friction and diffusion measurements.

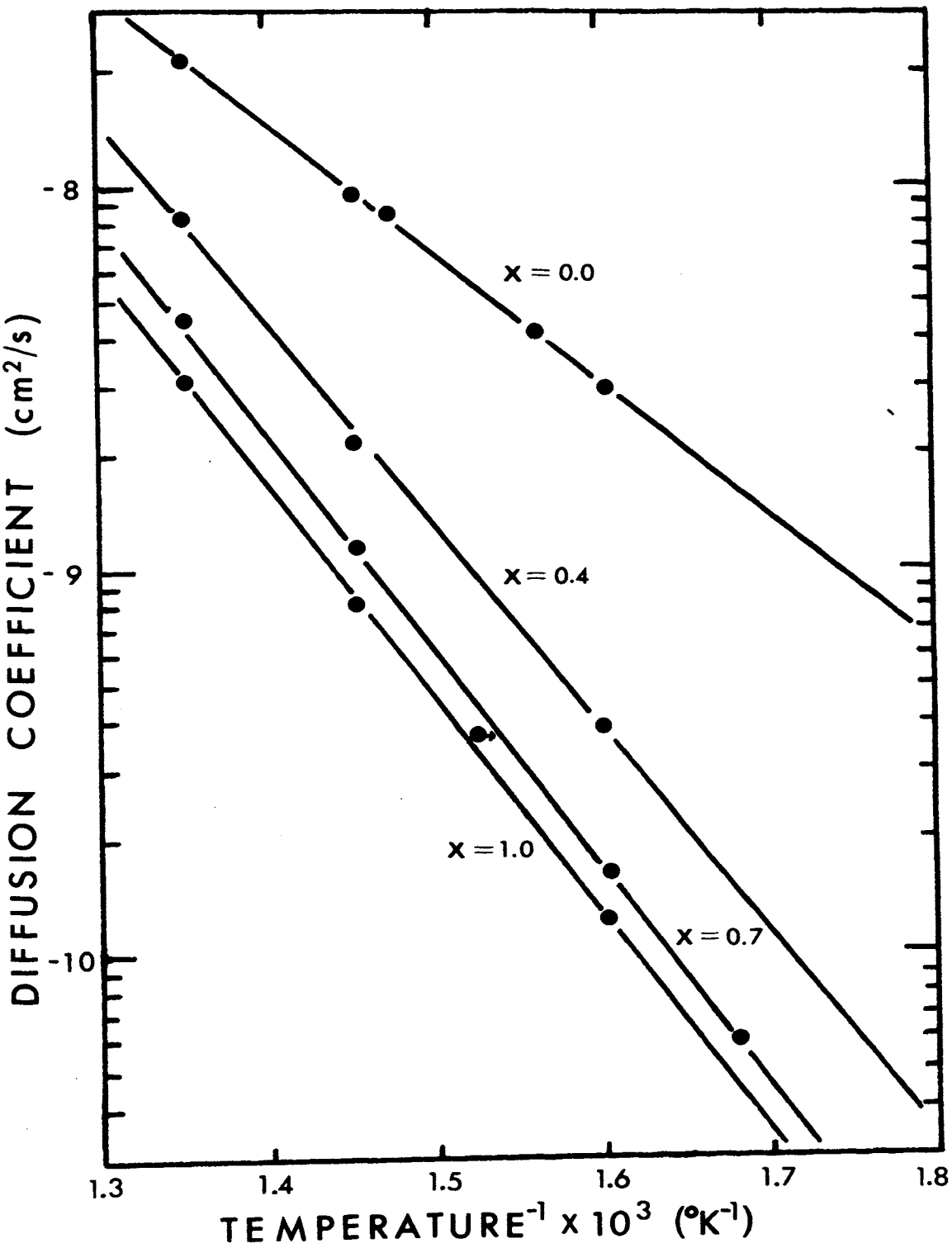

Figure 3. Temperature Dependence of Sodium Self-Diffusion in $(1-X)Na_2O \cdot XK_2O \cdot 3SiO_2$ Glasses.

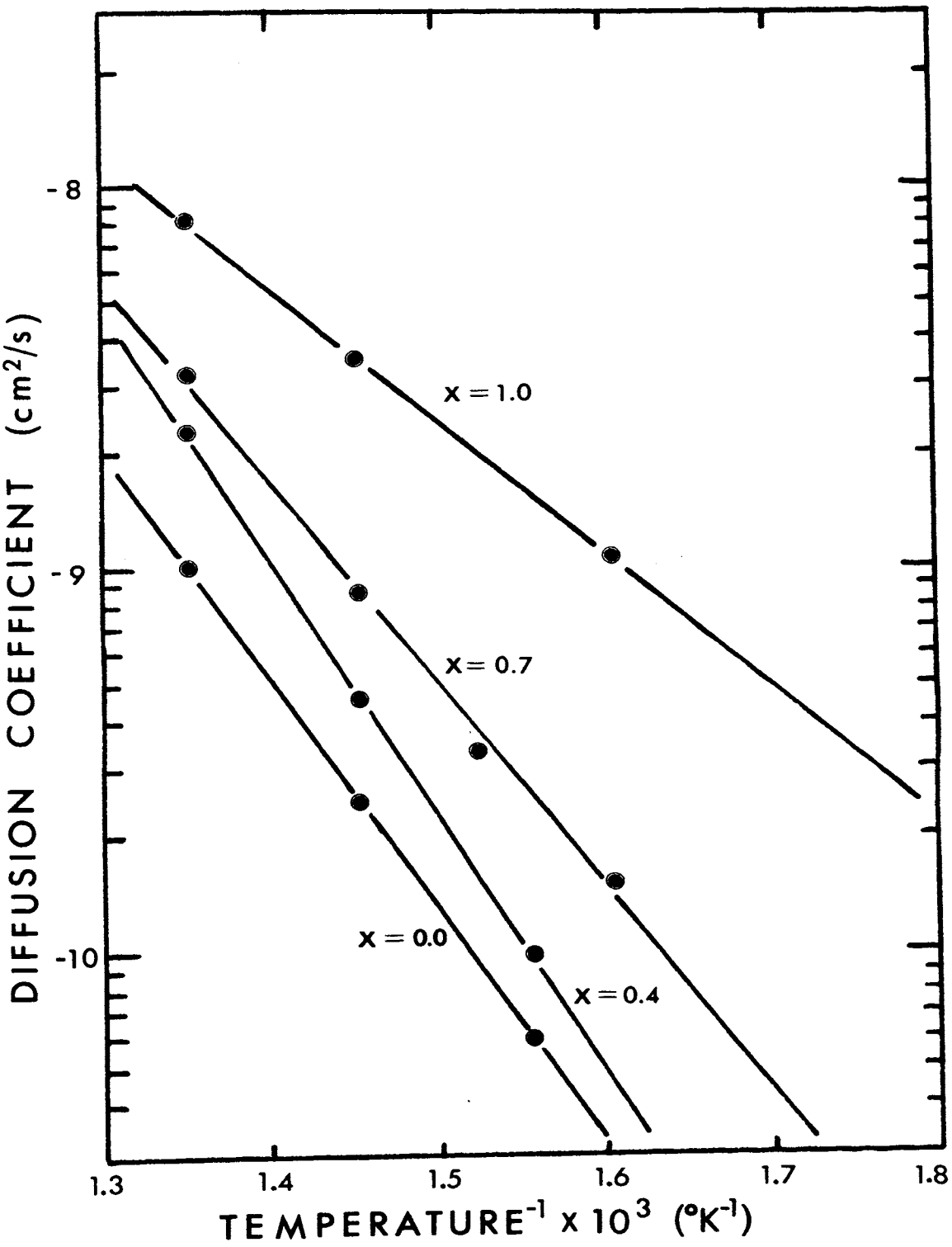

Figure 4. Temperature Dependence of Potassium Self Diffusion in $(1-X)Na_2O \cdot XK_2O \cdot 3SiO_2$.

TABLE IV

Self-Diffusion Coefficients (cm^2/sec), Activation Energies, and Preexponential Factors for Sodium and Potassium Diffusion in $(1-X)Na_2O \cdot XK_2O \cdot 3SiO_2$ Glasses

X	Temperature (°C) 250	350	400	450	E(±1) Kcal/mole	D_o cm^2/sec
			Sodium			
0.00	2.72×10^{-10}	2.98×10^{-9}	7.57×10^{-9}	1.68×10^{-8}	15.4	8.19×10^{-4}
0.40	8.31×10^{-12}	3.60×10^{-10}	1.56×10^{-9}	5.50×10^{-9}	24.3	1.30×10^{-1}
0.70	2.78×10^{-12}	1.55×10^{-10}	7.43×10^{-10}	2.86×10^{-9}	25.9	2.14×10^{-1}
1.00	2.29×10^{-12}	1.19×10^{-10}	5.52×10^{-10}	2.07×10^{-9}	25.5	1.09×10^{-1}
			Potassium			
0.00	4.11×10^{-13}	2.97×10^{-11}	1.57×10^{-10}	6.60×10^{-10}	27.6	1.59×10^{-1}
0.40	4.05×10^{-13}	4.56×10^{-11}	2.85×10^{-10}	1.39×10^{-9}	30.4	2.43
0.70	3.26×10^{-12}	1.39×10^{-12}	6.00×10^{-10}	2.11×10^{-9}	24.2	4.77×10^{-2}
1.00	9.47×10^{-11}	1.08×10^{-9}	2.79×10^{-9}	6.31×10^{-9}	15.7	3.71×10^{-4}

IV. DISCUSSION

A. Activation Energies for Alkali Diffusion and Mixed-Alkali Peak

Figure 5 shows how the activation energies for sodium and potassium diffusion and for mixed-alkali internal friction change with composition. As previously reported for similar Na-Rb glasses,[7] there is no apparent correlation between the activation energy for the mixed-alkali peak and that for either Na or K diffusion. If the mixed-alkali peak depended upon the mobility of a single alkali as does the alkali peak,[14-16] then a correlation between the activation energy for single alkali diffusion and mixed-alkali peak would be expected. The relaxation mechanism responsible for this peak is apparently more complicated, and as suggested by McVay and Day,[7] "a cooperative movement of both alkali ions... could account for this lack of agreement between the activation energies."

The activation energies for diffusion and for the mixed-alkali peak are equal, within experimental error, at the composition exhibiting the maximum peak height, $K/Na + K = 0.64$. No significance is attached to this similarity, however, since the activation energies in the Na-Rb glasses were dissimilar. In the Na-Rb glasses the activation energy for diffusion and that for the mixed-alkali peak differed by about 4 kcal at the composition where the peak height was a maximum, i.e., Rb/Na +

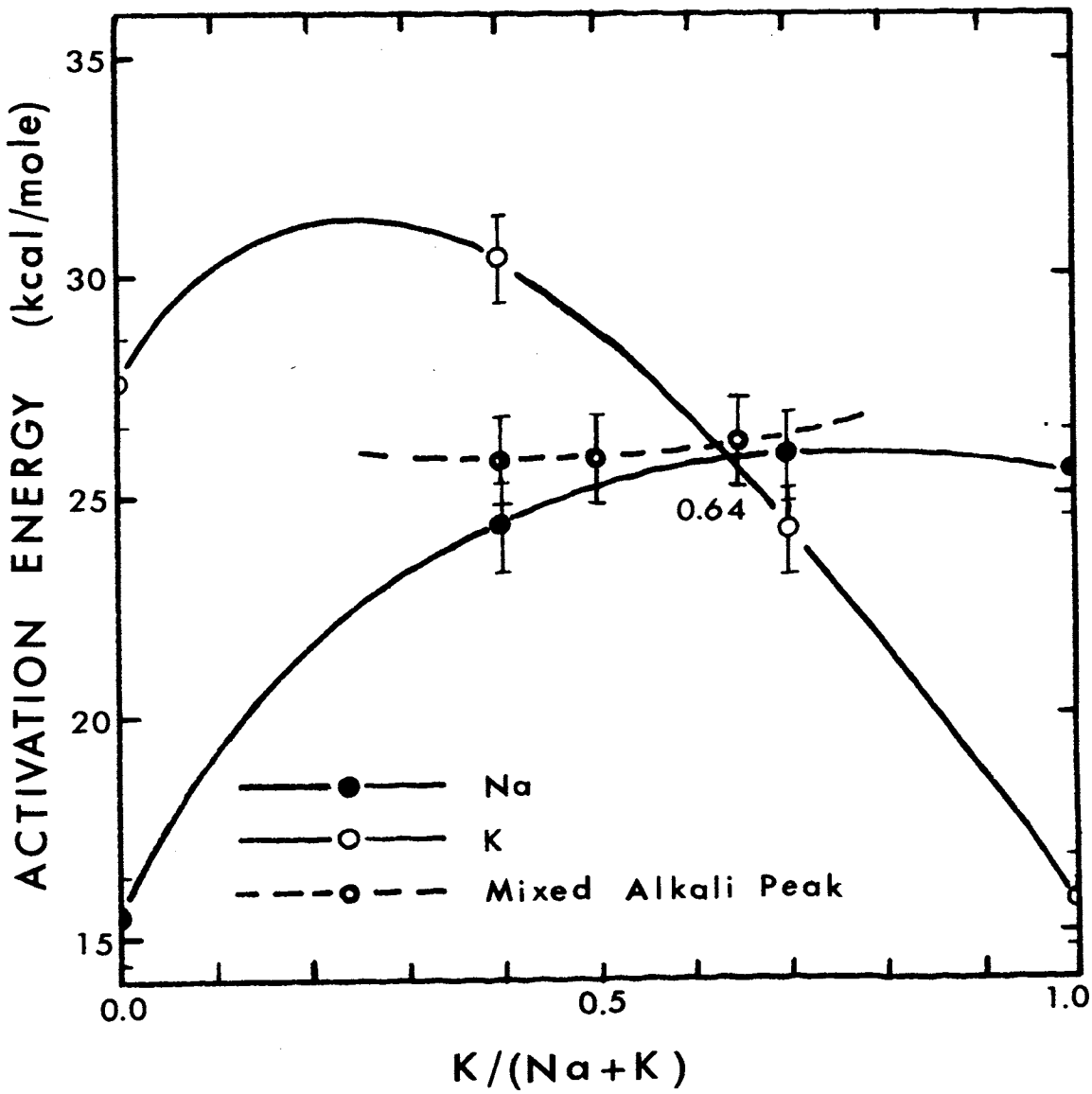

Figure 5. Activation Energy for Alkali Diffusion and the Mixed-Alkali Internal Friction Peak in $(1-X)Na_2O \cdot XK_2O \cdot 3SiO_2$ Glasses.

Rb = 0.70.

B. Correlation Between Diffusion Coefficient and Mixed-Alkali Peak

For any given temperature the self-diffusion coefficients for the dissimilar alkali in mixed-alkali glasses are equal at a certain composition. Figure 6 shows how the sodium and potassium self-diffusion coefficients vary with composition, for various temperatures, in $(1-X)Na_2O \cdot XK_2O3SiO_2$ glasses. This equality of the alkali diffusion coefficients at a particular composition has also been reported in Na-Rb silicate,[7] Na-K silicate,[8] Na-K lime silicate,[9] Na-Cs silicate,[17] and Na-Rb germanate[10] glasses. On the basis of these studies it is concluded that different mixed-alkali compositional systems will contain a particular composition at which the two alkalis have the same diffusion coefficient. The composition at which the alkali diffusion coefficients are equal will hereafter be denoted as C.I.

It is important to note from Figure 6 that the C.I. moves to higher potassium concentrations with increasing temperatures. Movement of the C.I. to higher concentrations of the larger ion, with increasing temperature, is also evident in Na-K lime silicate glasses[9] and Na-Rb germanate glasses.[10] Lacharme[9] measured the Na and K diffusion coefficients between 350 and 500°C in glasses containing 13.2 mole % total alkali. An ion exchange technique, utilizing radioactive Na^{24} and K^{42} was employed.

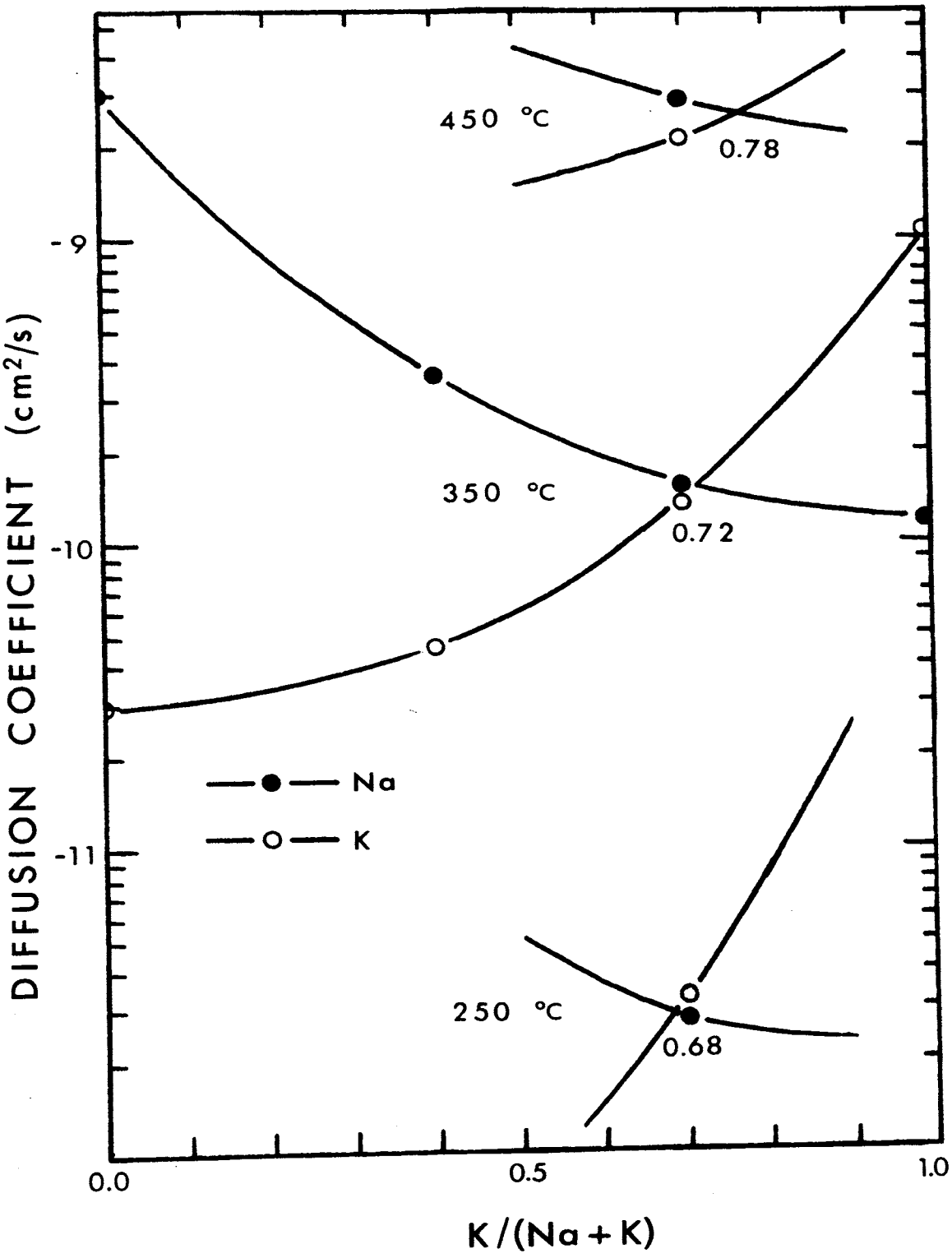

Figure 6. Self-Diffusion Coefficients for Sodium and Potassium in $(1-X)Na_2O \cdot XK_2O \cdot 3SiO_2$ Glasses.

At 394°C the C.I. occurred at a K/Na+K ratio of 0.90. At 447°C the C.I. was located at(K/Na + K)= 0.94. Evstropév and Pavlovski[10] determined the Na and Rb diffusion coefficients between 300 and 450°C in (1-X) $Na_2O \cdot XRb_2O \cdot 3GeO_2$ glasses utilizing radioactive Na^{22} and Rb^{86} with a sectioning technique. Their data indicate that the C.I. moves from X=0.78 at 300°C to X=0.85 at 400°C.

In contrast, the C.I. in $(1-X)Na_2O \cdot XRb_2O \cdot 3SiO_2$ glasses showed no detectable change between 350 and 500°C.[7] It is concluded that the C.I. should generally be expected to be temperature dependent and the Na-Rb silicate glasses represent a unique case, to be discussed later.

In the temperature range where the mixed-alkali peak has been measured in $(1-X)Na_2O \cdot XK_2O \cdot 3SiO_2$ and $(1-X)Na_2O \cdot XRb_2O \cdot 3SiO_2$ glasses, the C.I. is the same composition at which the mixed-alkali internal friction peak is a maximum. In the (1-X) $Na_2O \cdot XK_2O \cdot 3SiO_2$ glasses the C.I. is at X=0.68 at 250°C and the maximum peak height occurs at X=0.65. In the $(1-X)Na_2O \cdot XRb_2O \cdot 3SiO_2$ glasses, the C.I., which is independent of temperature, is at X=0.73 and the maximum peak height occurs at X=0.70. These values are considered the same, within experimental error.

The observed temperature dependence for the C.I. in certain mixed-alkali glasses could account for the dis-

crepancy between the diffusion and internal friction data in the $(1-X)Na_2O \cdot XK_2O \cdot 4SiO_2$ glasses. The diffusion data reported by Evstropév shows that the C.I. occurs at a K/Na + K ratio of 0.77, at 415°C, whereas the maximum height for the mixed-alkali peak occurred at K/Na + K = 0.63 as measured at 125°C by the present authors. On the basis of the present study it is proposed that diffusion measurements at lower temperatures would show the C.I. shifting to lower values for the K/Na + K ratio. It is anticipated, therefore, that diffusion and internal friction measurements made at approximately the same temperature would show that the maximum peak height and C.I. occur at the same composition.

It is expected that the correlation between the C.I. and the maximum height for the mixed-alkali peak in the $(1-X)Na_2O \cdot XK_2O \cdot 3SiO_2$ and $(1-X)Na_2O \cdot XRb_2O \cdot 3SiO_2$ glasses should also apply to other mixed-alkali glasses exhibiting a mixed-alkali peak. This indicates that the mobility of the alkali ions influences the mixed-alkali peak and is, therefore, consistent with the proposed mechanism for this damping maximum.

The temperature dependence for the C.I. suggests that the composition at which the mixed-alkali peak is a maximum should also change with temperature. Internal friction measurements made in the $(1-X)Na_2O \cdot XK_2O \cdot 3SiO_2$ glasses at higher frequencies, thereby shifting the mixed-alkali peak to higher temperatures, Table III, showed no

change in the composition at which the mixed-alkali peak is a maximum. The fact that the maximum peak height remained at X=0.65 when the mixed-alkali peak was shifted from 115°C to 240°C (by changing the frequency of measurement) is attributed to the small temperature dependence for the C.I. at low temperatures.

The diffusion measurements in the present study and those for Na-K lime silicate glasses[9] both indicate that the change in C.I. for a given change in temperature is larger at high temperature (>300°C) than at low temperatures (<300°C). For example, no change in the C.I. was detectable from 352 to 394°C in the Na-K lime silica glasses[9] but from 394 to 447°C it shifted 4 mole % K_2O, i.e., from X=0.90 to 0.94. Similarly, the C.I. in Figure 6 changed about 4 mole % K_2O (from X=0.68 to X=0.72) from 250° to 350°C, but from 350° to 450°C it changed about 6 mole % K_2O (from X=0.72 to X=0.78).

Figure 7 shows how the C.I., as calculated from the diffusion measurements, varies with temperature for the Na-K glasses. In the temperature range over which the mixed-alkali peak was measured, 115 to 240°C, the C.I. changes from approximately X=0.65 to 0.67. This small change is believed to be the reason why the internal friction measurements at low and high frequencies (or temperatures) did not show any change in the composition corresponding to maximum peak height, X=0.65.

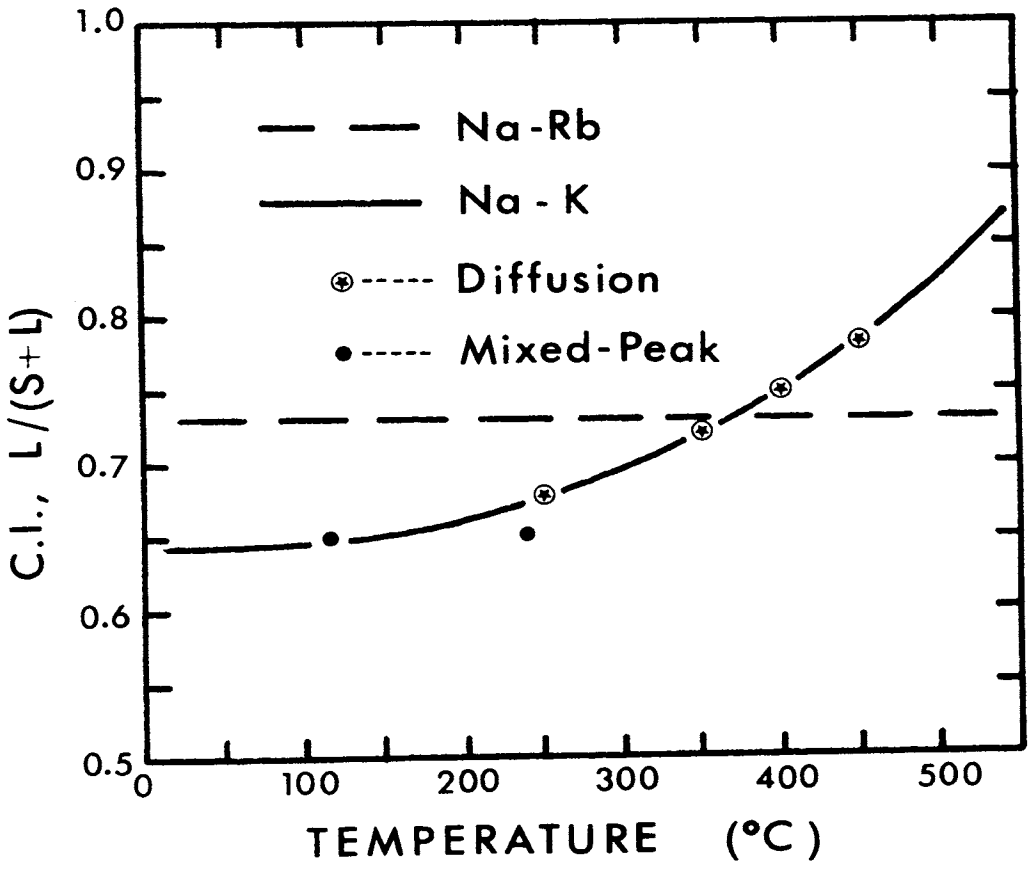

Figure 7. Change in composition where $D_L=D_S$ (C.I.) with temperature for $(1-X)Na_2O \cdot XK_2O \cdot 3SiO_2$ and $(1-X)Na_2O \cdot XRb_2O \cdot 3SiO_2$ (McVay and Day) glasses. (⊛) determined from alkali diffusion measurements, and (●) composition where mixed-alkali peak is maximum for the Na-K glasses.

C. Comparison of Mixed-Alkali Systems

The correlation between the diffusion coefficient for the slower moving ion and the mixed-alkali peak previously reported[7] for $(1-X)Na_2O \cdot XRb_2O \cdot 3SiO_2$ glasses also exists for the $(1-X)Na_2O \cdot XK_2O \cdot 3SiO_2$ glasses.

In Figures 8 and 9 the alkali diffusion coefficients and the mixed-alkali peak height are compared for the Na-Rb and Na-K glasses. For any given alkali ratio, the glass having the larger diffusion coefficient for the slower moving alkali (D_{slow}), at a given temperature, also exhibits a larger mixed-alkali peak. Consider, for example, the glasses with an alkali ratio of 0.40. At 350°C K and Rb are the slower moving alkali in Na-K and Na-Rb glasses, respectively. The diffusion coefficient for K is 4.56×10^{-11} and that for Rb is 2.1×10^{-12} cm^2/sec. Correspondingly, the mixed-alkali peak height in the Na-K glass is 28.2×10^{-3} as compared to 19.0×10^{-3} for the Na-Rb glass. For glasses having an alkali ratio of 0.80 the slower moving alkali in both the Na-K and Na-Rb glasses at 350°C is sodium. D_{Na} equals 1.35×10^{-10} and 1.15×10^{-11} cm^2/sec in the Na-K and Na-Rb glasses, respectively. The mixed-alkali peak height again corresponds to the relative mobility being 26.5×10^{-3} and 22.0×10^{-3} for the Na-K and Na-Rb glasses, respectively. Other comparisons could be made, but it should be clear that the magnitude of the mixed-alkali peak varies closely with the magnitude of the diffusion coefficient for the

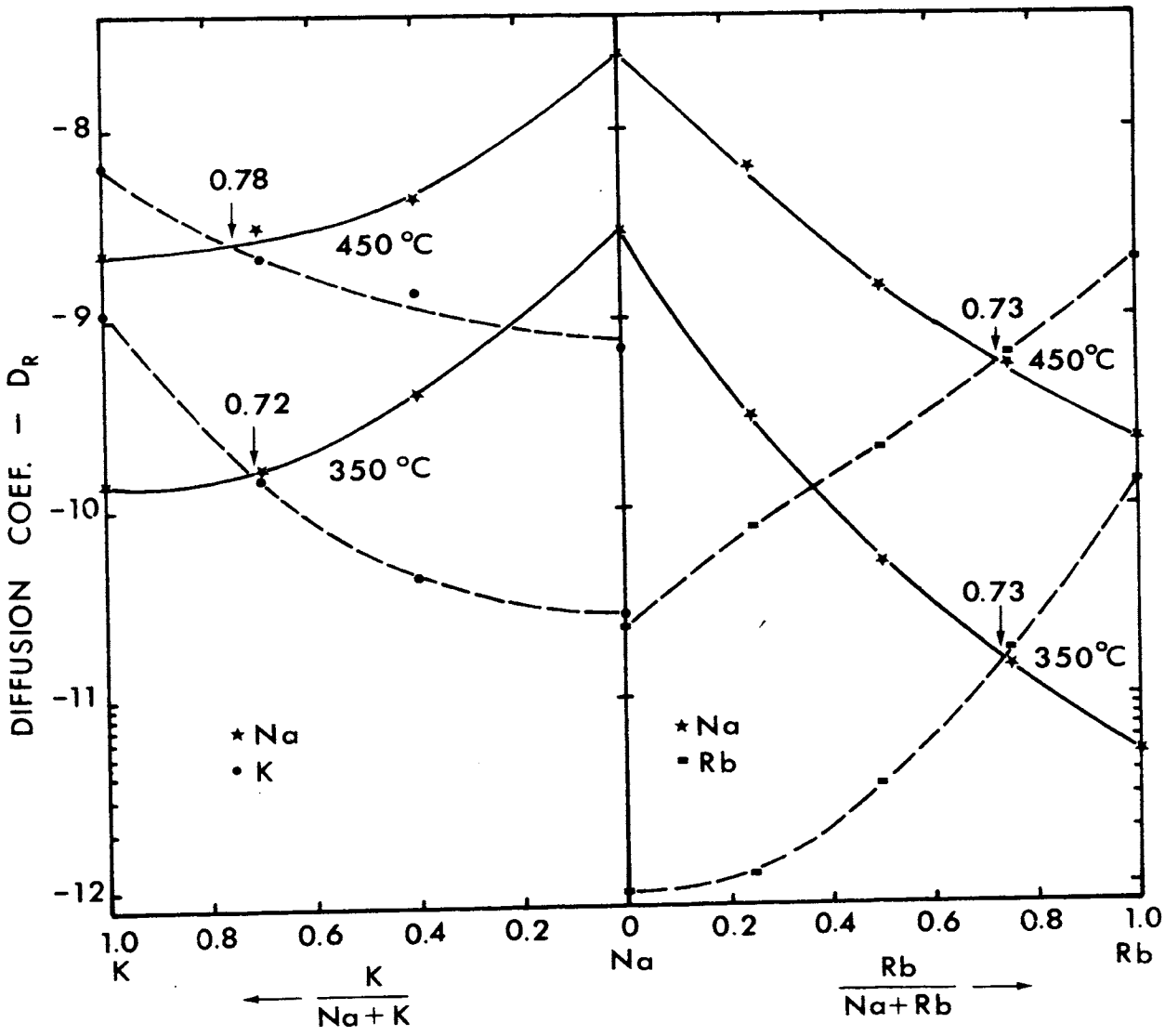

Figure 8. Alkali Diffusion Coefficients in (1-X) $Na_2O \cdot XK_2O \cdot 3SiO_2$ (left side) and (1-X) $Na_2O \cdot XRb_2O \cdot 3SiO_2$ (McVay and Day, right side) Glasses.

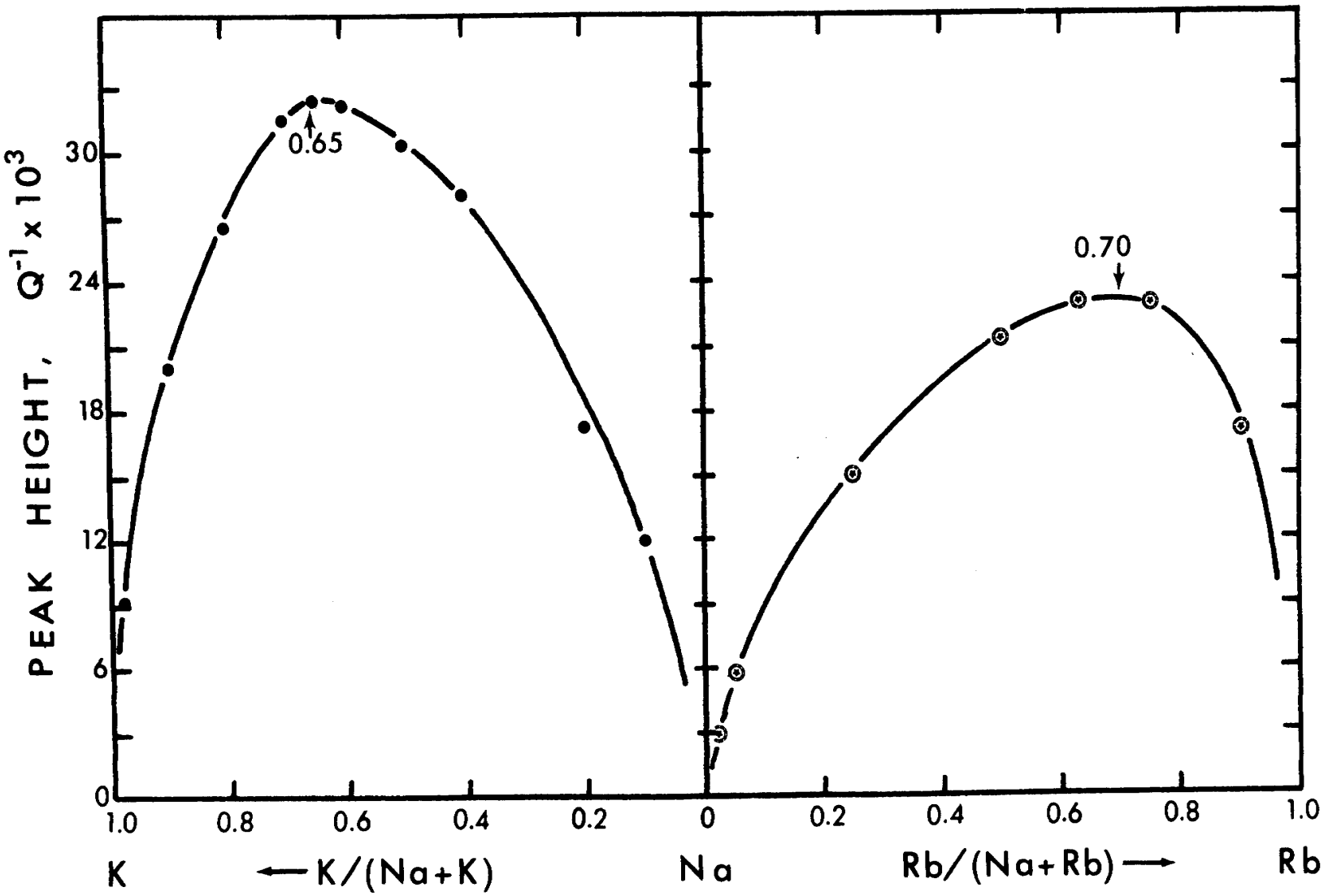

Figure 9. Mixed-Alkali Peak Height for $(1-X)Na_2O \cdot XK_2O \cdot 3SiO_2$ (left side) and $(1-X)Na_2O \cdot XRb_2O \cdot 3SiO_2$ (McVay and Day, right side) Glasses.

slower moving ion.

It is also evident that the glass having the larger diffusion coefficient at the C.I. (for any given temperature) also exhibits the larger mixed-alkali peak. The diffusion coefficients at the C.I. for Na-K and Na-Rb are 1.5×10^{-10} and 1.5×10^{-11} cm^2/sec, respectively. Correspondingly the maximum mixed-peak heights are 32.6×10^{-3} and 24.0×10^{-3}.

Because of limited internal friction and diffusion data, comparisons between other mixed-alkali systems are not as comprehensive as that between the Na-K and Na-Rb glasses. However, information allowing partial comparisons between the mixed-alkali peak and alkali diffusion for different mixed-alkali glasses has been assembled in Table V.

There is a general correspondence between the value for D_{slow} and the magnitude for the mixed-alkali peak. This correspondence is not meant to imply that the mixed peak height increases exponentially with temperature as is the case for the diffusion coefficient. Consequently, all comparisons should be made at an arbitrarily selected, but constant temperature. The basic significance between the alkali diffusion coefficients and the height for the mixed-alkali peak is not known. However, it is clear that changes in the height of the mixed-alkali peak accurately reflect changes in alkali mobility resulting from changes in composition.

TABLE V

Diffusion and Internal Friction Data for Various Mixed-Alkali Glasses

		Na-K $3SiO_2$ (*)	Na-Rb $3SiO_2$ (7)	Na-K $4SiO_2$ (8)	Na-Cs $5SiO_2$ (17)
L/(S+L) at which $D_L=D_S$	400°C	0.75	0.73		0.83
	415°C	0.76	0.73	0.77	
L/(S+L) at which mixed peak is maximum		0.65(240°C)	0.70	0.63(125°C)	
		0.65(115°C)	(310-140°C)		
D at $D_L=D_S$ (cm^2/sec)	400°C	6.9×10^{-10}	1.1×10^{-10}		3.0×10^{-12}
	415°C	1.0×10^{-9}	1.8×10^{-10}	3.2×10^{-10}	
D_{slow} at L/(S+L)=0.5 (cm^2/sec)	400°C	3.5×10^{-10}	3.1×10^{-11}		1.2×10^{-13}
	415°C	5.2×10^{-10}	5.0×10^{-11}	3.2×10^{-10}	
Maximum Mixed Peak Height		32.6×10^{-3}	2.4×10^{-3}	25.0×10^{-3}	
Mixed Peak Height for L/(S+L) = 0.5		30.3×10^{-3}	21.3×10^{-3}	24.0×10^{-3}	14.1×10^{-3} (in $3SiO_2$)

L/(S+L) = Alkali ratio, large and small ion denoted by L and S, respectively

D_L and D_S denoted diffusion coefficients for large (L) and small (S) ion

* Present investigation

D. Temperature Dependence of Compositions Where $D_L=D_S$

The alkali self-diffusion coefficients in the (1-X) $Na_2O \cdot XRb_2O \cdot 3SiO_2$ glasses showed no detectable variation in the C.I. at different temperatures. Since temperature dependence has been found in the Na-K silicate, Na-K lime silicate, and Na-Rb germanate glasses it appears that either the Na-Rb silicate glasses don't show this temperature dependence, except at higher temperatures, or they represent a special case.

The temperature (T_I) at which the diffusion coefficients are equal for any given composition (C.I.) can be determined by solving the two linear equations obtained from equation (4):

$$\ln D_S = \ln D_{oS} - E_S/RT \qquad (5)$$

$$\ln D_L = \ln D_{oL} - E_L/RT \qquad (6)$$

The subscripts S and L represent the small and large alkali ion respectively. Solving equations 5 and 6, the equation for T_I for any given alkali ratio (value of X) becomes:

$$T_I \Big|_X = \frac{E_S - E_L}{R\,(\ln D_{oS} - \ln D_{oL})} \qquad (7)$$

All four quantities, D_{oS}, D_{oL}, E_S, E_L, are compositionally dependent as illustrated in Figures 5 and 10. Values from these figures for any given alkali ratio, X=K/Na + K, can be used in equation (7) to determine T_I for that composition.

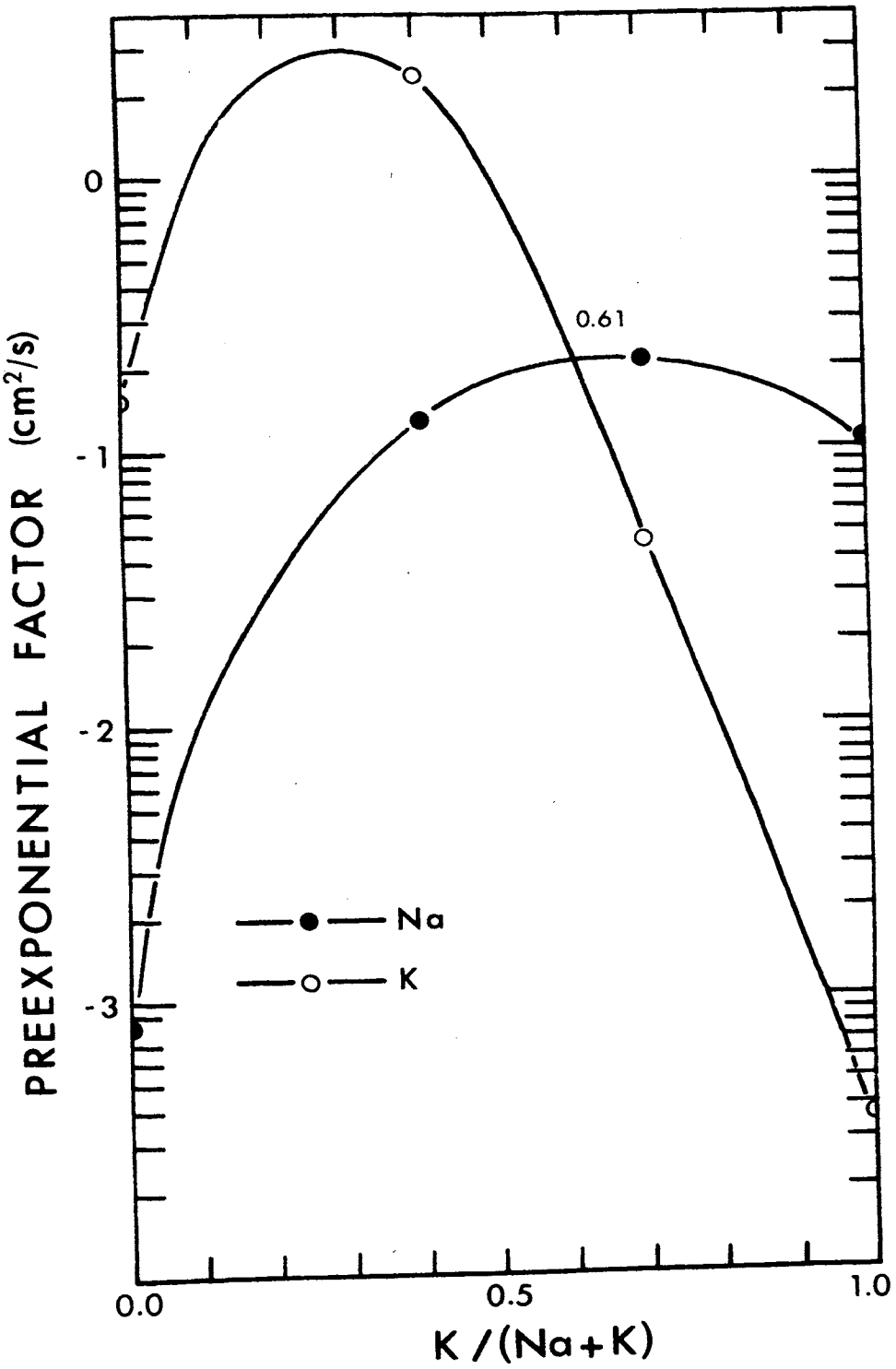

Figure 10. Pre-Exponential Factor (D_o) for Alkali Diffusion in $(1-X)Na_2O \cdot XK_2O \cdot 3SiO_2$ Glasses.

Figure 11 is an example of how T_I is obtained from equations (5) and (6), the intersection of the two lines indicating the T_I for that composition.

There are two special cases where equation 7 is not directly applicable. The first is when $E_S = E_L$ in a particular composition. In this case D_{Na} and D_K in Figure 11 would be represented by two parallel lines and there would be no intersection. The second case is when $E_S = E_L$ and $D_{oS} = D_{oL}$ for a certain composition. In this case D_{Na} and D_K in Figure 11 would be represented by coincident lines and $D_{Na} = D_K$ at all temperatures. Only those interactions occurring at temperatures below the glass transition temperature are of interest in this investigation.

The temperatures at which the alkali diffusion coefficients are equal in the Na-K glasses, as calculated from equation 7, are shown in Figure 7. At temperatures below about 250°C, the C.I. changes only slightly, eventually becoming almost independent of temperature. There is a much larger change in the C.I. between 300 and 500°C.

Equation (7) cannot be used directly for the Na-Rb glasses since in these glasses $E_{Na} = E_{Rb}$ and $D_{oNa} = D_{oRb}$ at a Rb/Na + Rb ratio of 0.73 (special case #2). In other words, equations (5) and (6) are identical at this composition so $D_{Na} = D_{Rb}$ at all temperatures. (Calculations using data obtained from compositions other than

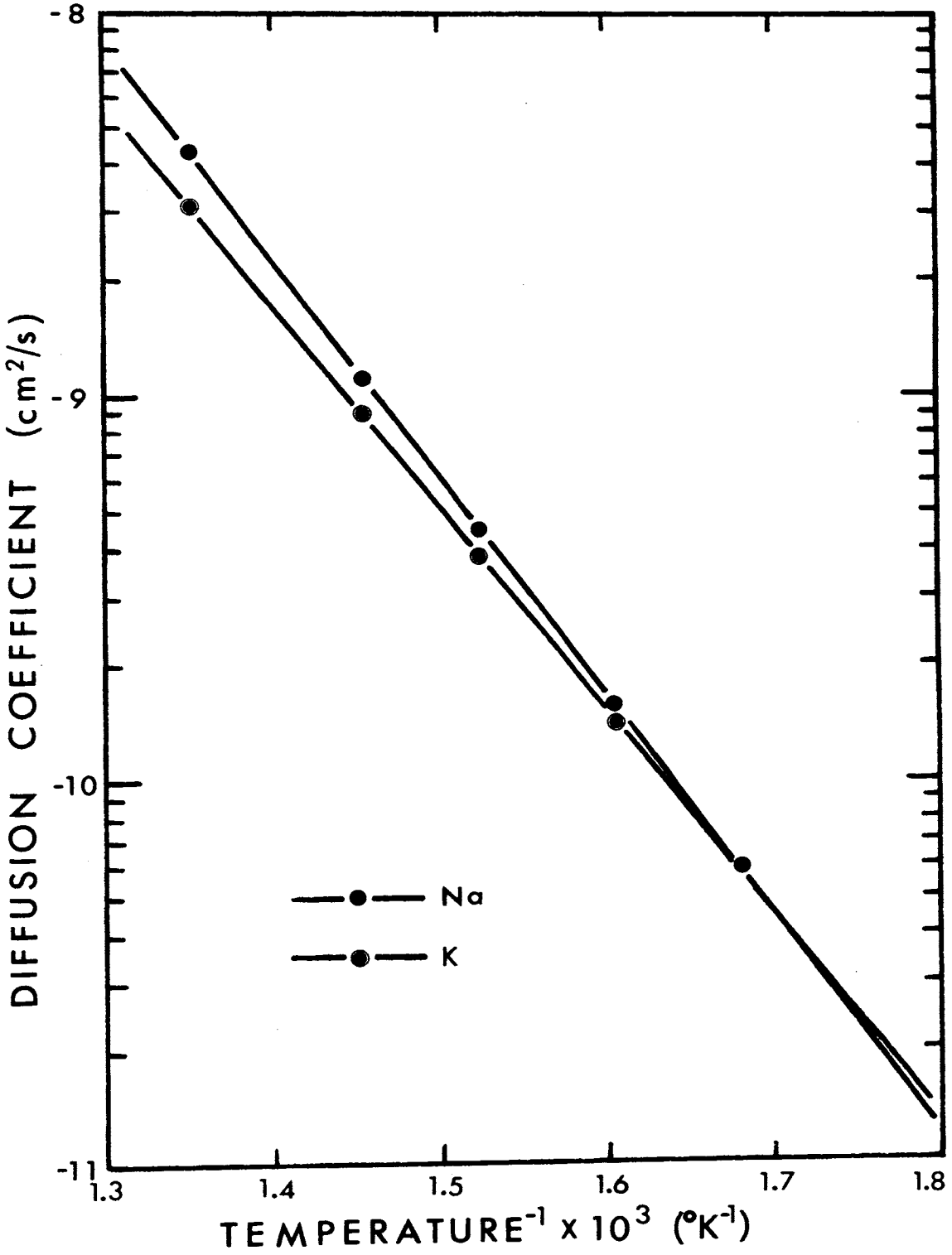

Figure 11. Temperature Dependence of Sodium and Potassium Self-Diffusion in $.30Na_2O \cdot .70K_2O \cdot 3SiO_2$ Glass.

X=0.73, i.e. X=0.80 indicate intersections well above the temperature range of interest.) Thus, the C.I. is independent of temperature as shown in Figure 7. The reason why the activation energies and pre-exponential terms are equal for sodium and rubidium in this particular composition, Rb/Na + Rb = 0.73, is not known. However, the absence of a temperature dependence for the C.I. in the Na-Rb glasses is considered unique and, in general, a temperature dependence is to be expected. The composition at which the two alkali diffusion coefficients will be equal at any given temperature is obviously determined by the compositional dependence of the pre-exponential and activation energy terms.

V. CONCLUSIONS

In glasses containing two dissimilar alkali there is a certain composition where the diffusion coefficients for the alkali are equal. In general, a temperature dependence for this composition should be expected.

It is concluded from comparisons made between mixed-alkali glasses containing two different alkali that the mixed-alkali internal friction peak is related to the alkali ion mobility. In the glasses studied the maximum magnitude for the mixed-alkali peak occurred at the composition where the alkali diffusion coefficients are equal. The magnitude for the mixed-alkali peak is more closely related to the slower moving alkali than to the faster moving alkali. At a given temperature the magnitude of the mixed-alkali peak gives an indication of the relative mobility of the slower moving ion in different mixed-alkali glasses. For example, for any given composition, the mixed-alkali peak height in $(1-X)Na_2O \cdot XK_2O \cdot 3SiO_2$ glasses is larger than that in $(1-X)Na_2O \cdot XRb_2O \cdot 3SiO_2$ glasses. Similarly, the diffusion coefficient of the slower moving ion at this temperature is also larger in the Na-K glasses than it is in the Na-Rb glasses.

There is no correlation between the activation energy for single alkali diffusion and that for the mixed-alkali peak. No significance is attached to the similarity between the activation energy for alkali diffusion and that for the mixed-alkali peak at X=0.65 in the (1-X)

$Na_2O \cdot XK_2O \cdot 3SiO_2$ glasses since the activation energies were different in the Na-Rb glasses.

The results of this study agree with the mechanism previously proposed for the mixed-alkali peak, i.e., a cooperative reorientation of the dissimilar alkali ions.

VI. APPENDICES

Sample Preparation and Heat Treatment

Appendix A

1. Glass Preparation and Melting

$(1-X)Na_2O \cdot XK_2O \cdot 3SiO_2$ and $(1-X)Na_2O \cdot XK_2O \cdot 4SiO_2$ glasses were prepared from reagent grade Na_2CO_3, K_2CO_3, and potter's flint (99.98% SiO_2). Because of the high viscosity of the melt .01 mole % KI was added to promote fining. Its contribution to the overall potassium content of the glass was considered in the batch calculation. The measured batch materials were mixed with enough acetone to create a slurry which was stirred continuously until the batch was nearly dry. It was then kept in a dryer until the first charge was made.

A platinum crucible was preheated to about 1400°C in an electric furnace open to the atmosphere. Small charges of the dried batch were made at intervals allowing enough time for melting between charges. The remainder of the batch was kept in the dryer between each charge.

After the final charge, the melt was heated to 1500°C and held there for five hours to allow fining. During this period the melt was stirred several times with a fused silica rod to assure homogeneity.

2. Sample Forming and Heat Treatment

Rectangular bars 1.3 x 1.3 x 15 and .65 x 1.3 x 15 cm. were made pouring the bubble free melt into stainless steel molds preheated to about 200°C. The bars were quickly

removed from the molds and placed in a furnace preheated to their respective annealing temperatures, see Table I. They were held at this temperature for four hours and then slowly cooled to room temperature.

Fibers approximately 0.5 mm in diameter were pulled from the same melt using a previously reported technique.[19] They were annealed at the appropriate temperature, Table I, for 30 minutes and slowly cooled to room temperature.

Internal Friction

Appendix B

1. Measurement

The apparatus used to measure internal friction at frequencies between .4 and 1.5 Hz. is an inverted torsion pendulum shown in Figure 13. This equipment and the measurement technique employed have been described elsewhere.[12,20] The temperature gradient during measurement never exceeded ± 2°C.

Internal friction at a frequency of approximately 1800 Hz, was measured by a resonance technique shown schematically in Figure 14. This technique is based on Förster's method[11] and has been reported previously.[13,21] The temperature gradient during measurement never exceeded ± 5°C.

2. Data

A summary of the internal friction data is given in Table III. Included in this table are the data obtained for the $(1-X)Na_2O \cdot XK_2O \cdot 4SiO_2$ glasses mentioned in preceding parts of this thesis.

Internal friction curves for each composition measured at a frequency of 0.8 Hz as shown in Figure 12. The composition exhibiting the maximum peak height for these glasses, X=0.63, was determined from a graph similar to Figure 1.

The height and temperature reported for the maximum

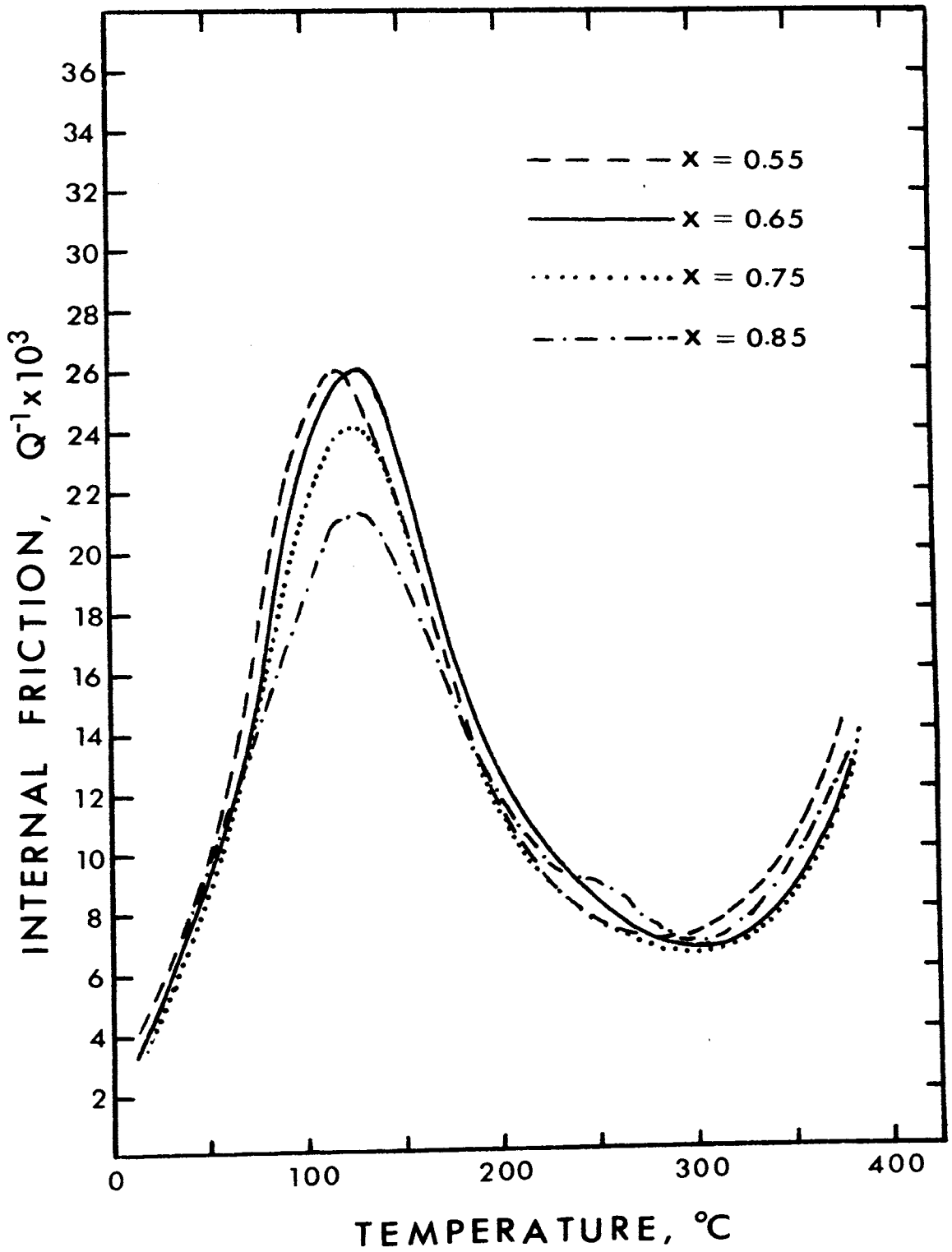

Figure 12. Internal Friction Curves for the (1-X) $Na_2O \cdot XK_2O \cdot 4SiO_2$ Glasses, Frequency 0.8 Hz.

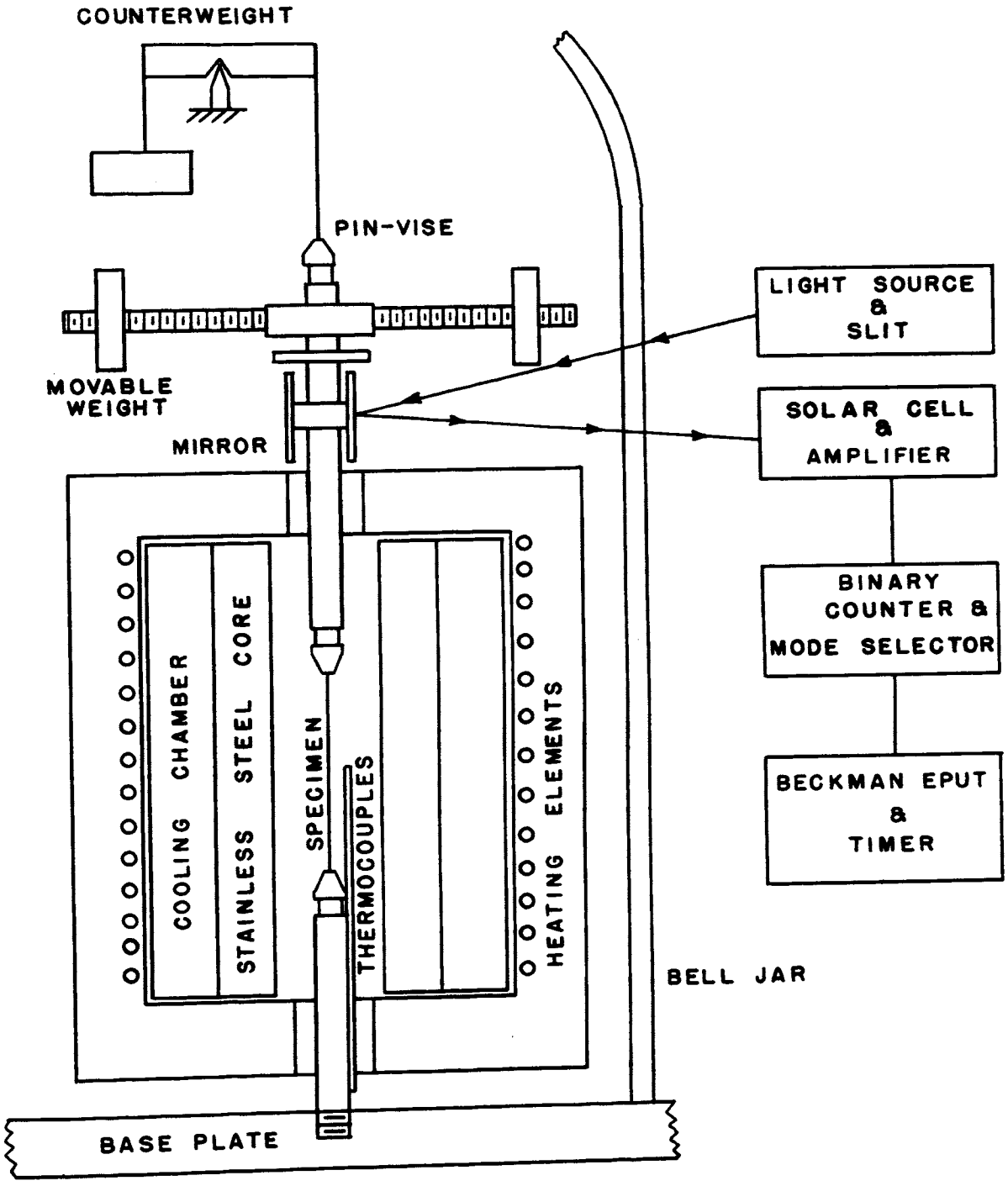

Figure 13. Inverted Torsion Pendulum and Furnace.

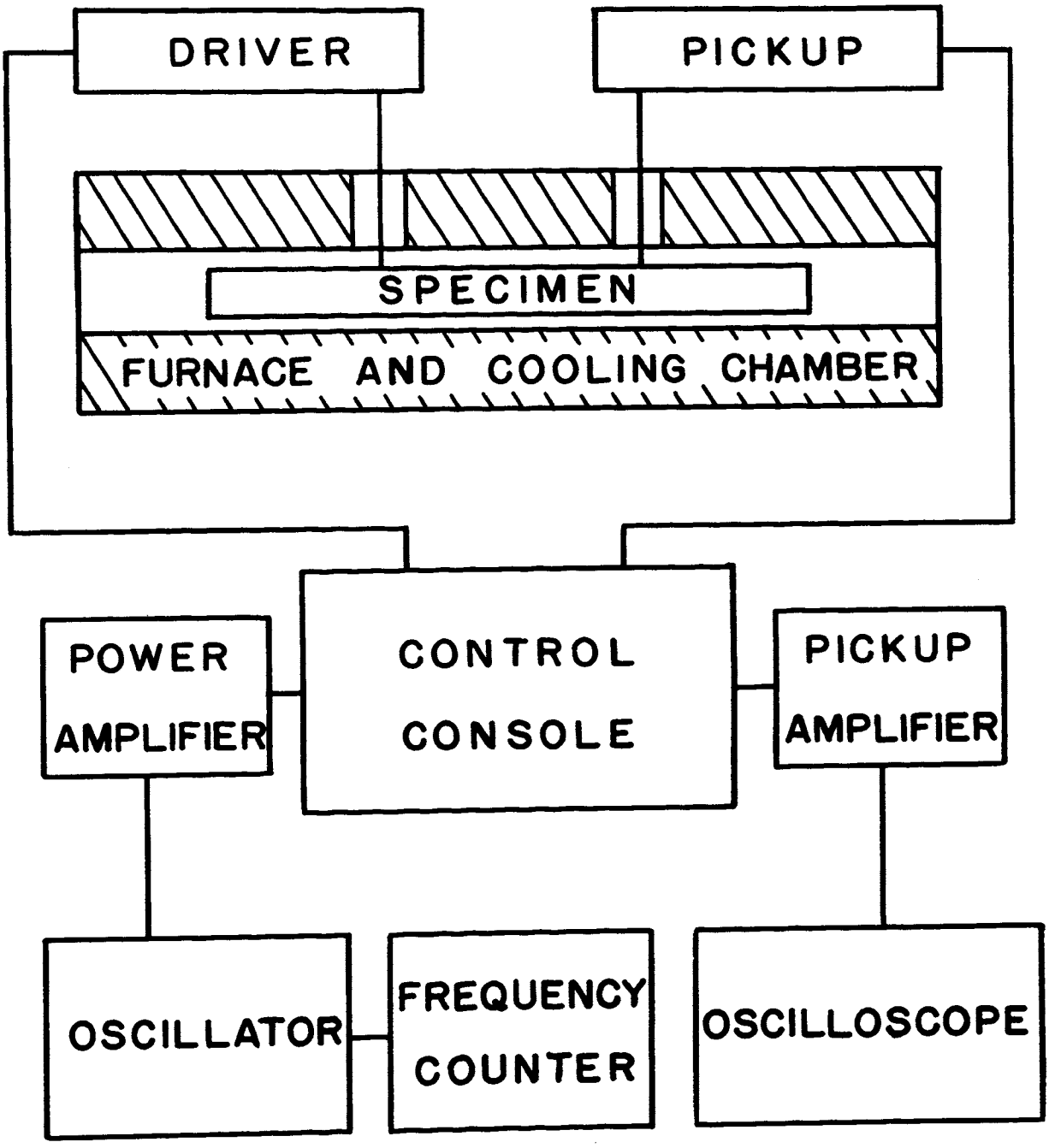

Figure 14. Block Diagram of Sonic Damping Equipment.

magnitude of an internal friction peak are dependent upon the designation of a background level. Since some of the internal friction data used in this study had been obtained by Shelby and Day,[5] their method of assigning background was also employed.[12]

The error in the determination of the composition exhibiting the maximum peak height is estimated to be ± 2 mole % total alkali.

Diffusion

Appendix C

1. Technique and Equipment

The self-diffusion coefficients of sodium and potassium were determined by using radioactive traces Na^{22} and K^{42} in a thin-sectioning technique, Figure 15. The technique and equipment have been described previously.[7,22] The glass density used for determining the section thickness, Table I, was measured by the Archimedes technique.[23]

2. Data

The experimental values for the self-diffusion coefficient of sodium and potassium ions at various temperatures are given in Table VI. These values were determined using a computer program designed to correct for the radioactive decay of the isotopes being measured while calculating the activity of the various sections.

The program then performed a least squares analysis on the data and used the corrected values in equation (1) to obtain a diffusion coefficient. When the diffusion coefficient was measured on duplicate samples, the average was reported. The simultaneously determined diffusion coefficients never differed by more than 10%.

A least squares program similar to that mentioned above was used to determine the best straight line fit to the diffusion data with respect to temperature^{-1}(°K).

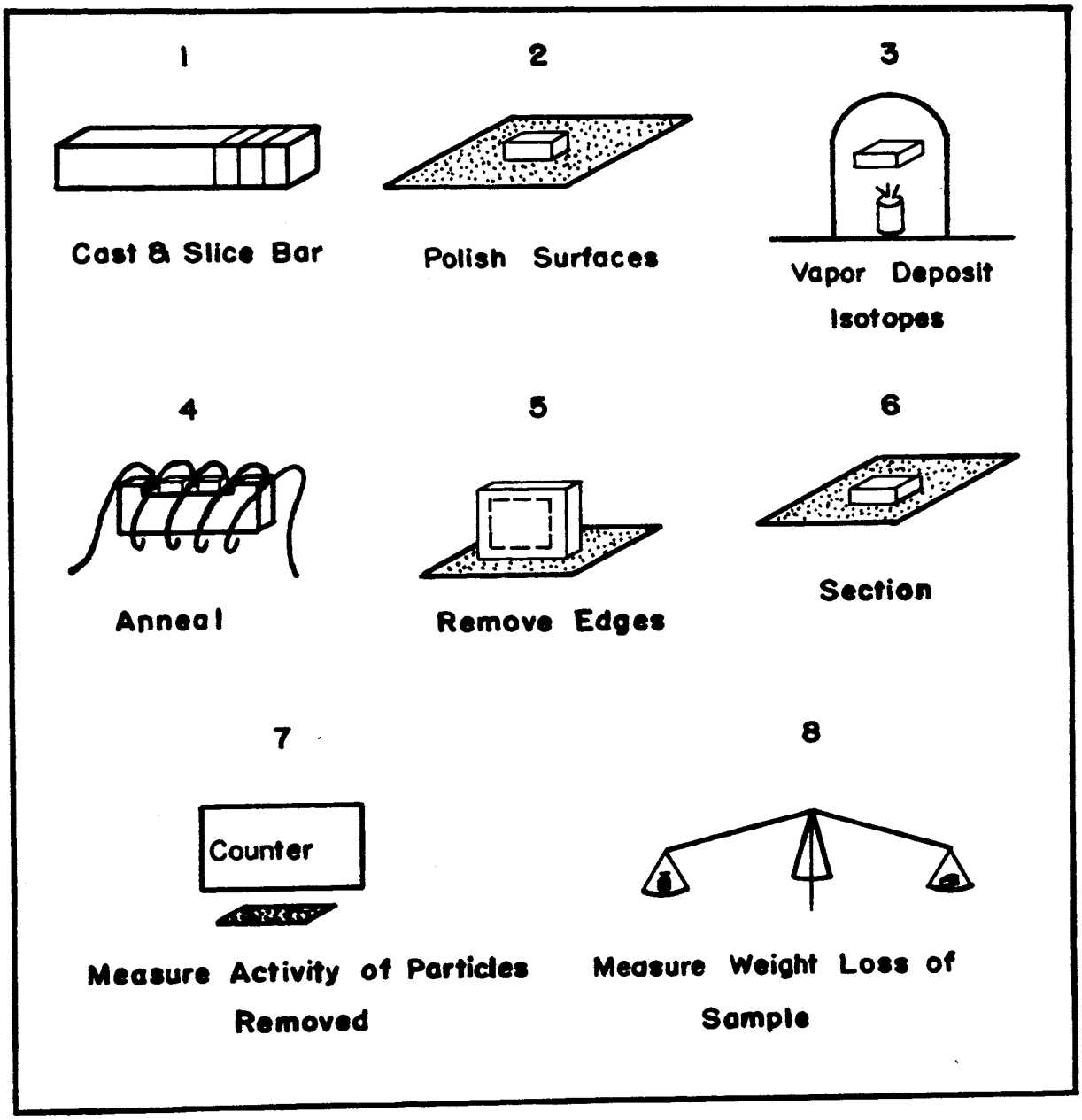

Figure 15. Procedure for Diffusion Measurements

TABLE VI

Experimental Data for the Self-Diffusion Coefficients of Sodium and Potassium

Glass	Diffusion Coefficient (cm^2/sec) D_{Na}^{22}	D_K^{42}	Temp (± 1/2°C)
$Na_2O \cdot 3SiO_2$	2.95×10^{-9}		350
	4.20×10^{-9}		367
	8.70×10^{-9}		405
	9.50×10^{-9}		415
	2.15×10^{-8}		467
		5.98×10^{-11}	370
		2.50×10^{-10}	415
		1.03×10^{-9}	467
$.60Na_2O \cdot 40K_2O \cdot 3SiO_2$	3.99×10^{-10}		352
	2.13×10^{-9}		415
	8.59×10^{-9}		467
		1.00×10^{-10}	370
		4.60×10^{-10}	415
		2.30×10^{-9}	467
$.3Na_2O \cdot 7K_2O \cdot 3SiO_2$	6.08×10^{-11}		322
	1.66×10^{-10}		350
	3.74×10^{-10}		383
	1.16×10^{-9}		415
	4.64×10^{-9}		467
		1.54×10^{-10}	350
		3.31×10^{-10}	383
		8.77×10^{-10}	415
		3.30×10^{-9}	467
$K_2O \cdot 3SiO_2$	1.25×10^{-10}		351
	8.15×10^{-10}		415
	3.17×10^{-9}		467
		1.10×10^{-9}	350
		3.53×10^{-9}	415
		8.28×10^{-9}	467

Activation energies were calculated from the slope of this line in accordance with equation (4).

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VITA

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